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ORIGINAL ARTICLE

# Empirical modeling of drying kinetics and microwave assisted extraction of bioactive compounds from *Adathoda vasica* and *Cymbopogon citratus*

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**KEYWORDS**

Microwave assisted extraction;
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**Abstract** To highlight the shortcomings in conventional methods of extraction, this study investigates the efficacy of Microwave Assisted Extraction (MAE) toward bioactive compound recovery from pharmaceutically-significant medicinal plants, *Adathoda vasica* and *Cymbopogon citratus*. Initially, the microwave (MW) drying behavior of the plant leaves was investigated at different sample loadings, MW power and drying time. Kinetics was analyzed through empirical modeling of drying data against 10 conventional thin-layer drying equations that were further improvised through the incorporation of Arrhenius, exponential and linear-type expressions. 81 semi-empirical Midilli equations were derived and subjected to non-linear regression to arrive at the characteristic drying equations. Bioactive compounds recovery from the leaves was examined under various parameters through a comparative approach that studied MAE against Soxhlet extraction. MAE of *A. vasica* reported similar yields although drastic reduction in extraction time (210 s) as against the average time of 10 h in the Soxhlet apparatus. Extract yield for MAE of *C. citratus* was higher than the conventional process with optimal parameters determined to be 20 g sample load, 1:20 sample/solvent ratio, extraction time of 150 s and 300 W output power. Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy were performed to depict changes in internal leaf morphology.


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**Nomenclature**

$a$, $a_1$, $b$, $b_1$, $c$, $g$, $k$, $k_1$, $k_2$, $n$, $n_1$ empirical coefficients
$D_{eff}$ effective moisture diffusivity ($m^2 s^{-1}$)
$D_o$ pre-exponential factor ($m^2 s^{-1}$)
$E_a$ activation energy ($W g^{-1}$)
$k_o$ pre-exponential factor ($min^{-1}$)
$L$ half the thickness of the sample (m)
$m$ sample mass (g)
$M$ number of mathematical models used for empirical modeling
$MC_i$ moisture content at specific time (g water/g dry solids)
$MC_o$ moisture content at initial time (g water/g dry solids)
$MR$ moisture ratio
$N$ number of model constants
$P$ microwave output power (W)
$R^2$ coefficient of determination
$E_{RMS}$ root mean square error
$RSS$ residual sum of squares
$t$ drying time (min)
$W_c$ weights of the crude extract (g)
$W_o$ weight of dry powdered sample (g)

*Greek letters*
$\alpha$ constant ($min^{-1} m^{-2} s^{-1}$)
$\chi^2$ chi-square

*Subscripts*
$o$ initial
$i$ specific time
$th$ theoretical

## 1. Introduction

Auto-oxidation of food during transportation, storage and processing is the primary mechanism for its physical (taste, color) and nutritional deterioration [12]. There is growing interest in the food science community on bioactive components such as natural antioxidants and their potential to replace synthetic compounds[1] in various food applications. Since time immemorial, we have looked toward plants as a source of inspiration and for harnessing their medicinal properties; indeed, their contributions toward improving human health have been substantial [24]. In this vein, both *Adathoda vasica* and *Cymbopogon citratus* are well-recognized plants in the Indian system of oriental medicine [8,3]. The contemporary remedial applications of *A. vasica* include the treatment of asthma, chronic bronchitis, rheumatic inflammatory swellings, antispasmodics, piles, cold [6,14]. Identified *A. vasica* alkaloids, primarily, vasicine and vasicinone have been acknowledged to be bioactive with their combination producing both in vitro and in vivo bronchodilatory activity commensurate to that of theophylline [2,29]. Likewise, *C. citratus* (lemongrass) has been used in various pharmaceutical applications as spasmolytics, analgesics, antipyretics, and diuretics and in tranquilizers. Essential oil extract from lemongrass leaves has high citral content and is utilized as a raw material in the production of vitamin A, beta carotene, ionone, etc. [20].

In lieu of the shortcomings of conventional methods[2] toward bioactive component recovery from plants, research effort has been directed toward the applicability of newer techniques that utilize enzymes, microwaves, supercritical fluids and ultrasounds for assisting the extraction. In addition to their high safety-low cost aspect these processes also benefit from allowing extraction to occur without affecting the quality of the final product or degrading unsaturated compounds in the extract [4]. Particularly, Microwave Assisted Extraction (MAE) has shown promise with several studies demonstrating its feasibility for the extraction of compounds from medicinal plants [15,5,7]. MAE enhances traditional solvent extraction by subjecting the solvent to rapid heat generation and direct interaction with electromagnetic radiation. The process results in the creation of a high pressure difference that causes the plant cellular structure to break and the solvent to penetrate within its matrix [22].

A comprehensive understanding of both, the drying and extraction steps is necessary to design the extraction process, avoid the denaturation of the product and determine feasible operating parameters. Given the limited availability of this literature for *A. vasica* and *C. citratus*, this study investigates the effect of various process parameters on the leaf extraction yield of bioactive compounds therein. An empirical correlation was developed for the examined drying parameters by improvising upon a selected conventional drying model. A comparative experimental procedure was followed to distinguish conventional Soxhlet extraction and MAE which were performed following the microwave drying of the leaves.

## 2. Materials and methods

Fresh *A. vasica* and *C. citratus* leaves were sourced from the VIT University campus at Vellore, India (12°55′12.79″N – 79°7′59.9″E; 216 m above sea level). The leaves were washed with distilled water and stored at *ca* 10 °C. Both plant specimens were validated by the Plant Biotechnology Division[3] at VIT University, Vellore, India. Ten replicated measurements were performed to determine the leaf thickness using a micrometer (Leica stage micrometer-MA285, Germany) and initial moisture content by standard vacuum drying method. Leaf thickness was found to be 0.5 mm and 0.75 mm and moisture content was 70.72% and 68.75% (w.b.), for *A. vasica* and *C. citratus* respectively. All solvents and chemicals used in the study were purchased from SD Fine Chemicals, Mumbai, India, and were of analytical grade.

[1] *Inter alia*, synthetic antioxidants such as butylated hydroxyanisole have been banned in Japan and *tert*-butyl hydroquinone is no longer allowed for food applications in the EU and Canada.

[2] Such as hydrodistillation, enfleurage, maceration, pressing and distillation.

[3] http://www.vit.ac.in/academics/schools/sbst

### 2.1. Drying and extraction procedure

A programmable domestic microwave oven (CE108MDF, Samsung Electronic Instrument Co. Ltd, India) with inbuilt cavity of $358 \times 327 \times 231.5$ ($W \times D \times H$, mm), maximum power output of 900 W and a frequency of 2450 MHz was used to perform the drying experiments. Microwave (MW) drying of the leaves was investigated at different output powers (100, 180 and 300 W) as well as at various sample loadings (10, 20, 30, 40 and 50 g). The procedure has been described elsewhere [10]. Following this, MW dried leaves were ground with mortar and pestle. For conventional solvent extraction, MW dried leaves were packed in a thimble and extracted with 98.5% hexane (v/v) in a Soxhlet apparatus at 55 °C. A modified domestic microwave oven was used as detailed by Ratola et al. [21] for MAE. Extraction experiments were carried out in a round bottom flask (250 mL) that was placed within the microwave cavity at the same position for all the runs. For assisting the carryover of extraction vapors, a hole ($\phi$ 16 mm) was drilled on top of the oven and polypropylene tubes interconnected the extraction flask with an external water condenser (4 °C). The schematic for the experimental setup is shown in Fig. 1. Moreover, MAE was studied at varied microwave output power and dried leaf mass. The extract from both experimental methods was concentrated at 60 °C under reduced pressure in a rotary evaporator (BÜCHI Labortechnik AG, R-215, Switzerland) and the dried powder was collected in Eppendorf tubes. All the drying and extraction runs were performed in triplicate and average values have been reported here. Statistical analyses were performed using MATLAB® and the deviations were within 5%.

For *A. vasica* extraction, the solvent used was a mixture of hexane, acetone and ethanol in the ratio 2:1:1 (v/v); boiling point of the mixture is approximately 58 °C [13]. For *C. citratus* extraction, hexane alone was used (based on preliminary studies). To examine the effect of sample loading and solvent volume on the extraction, sample mass to solvent ratio was varied as 1:10, 1:15 and 1:20. The extract yield obtained was calculated using Eq. (1) where, $W_c$ and $W_o$ are the weights of the crude extract (g) and the weight of dry powdered sample (g) respectively.

$$\text{Yield}(\%) = \frac{W_c}{W_o} \cdot 100 \quad (1)$$

### 2.2. Mathematical modeling and drying kinetics

To design a suitable dryer for the investigated leaves, the analysis of drying kinetics and its mathematical modeling is essential [25]. The drying data were tested against ten well-known thin-layer drying models with the equation parameters determined using nonlinear regression analysis [28] (Table 1). The moisture content of the leaves at equilibrium was assumed to be zero allowing the simplification of the Moisture Ratio ($MR$) as $MC_i/MC_o$ [9]; $MC_i$ is the moisture content at time '$i$' and $MC_o$ is the moisture content at initial time '$o$' in g

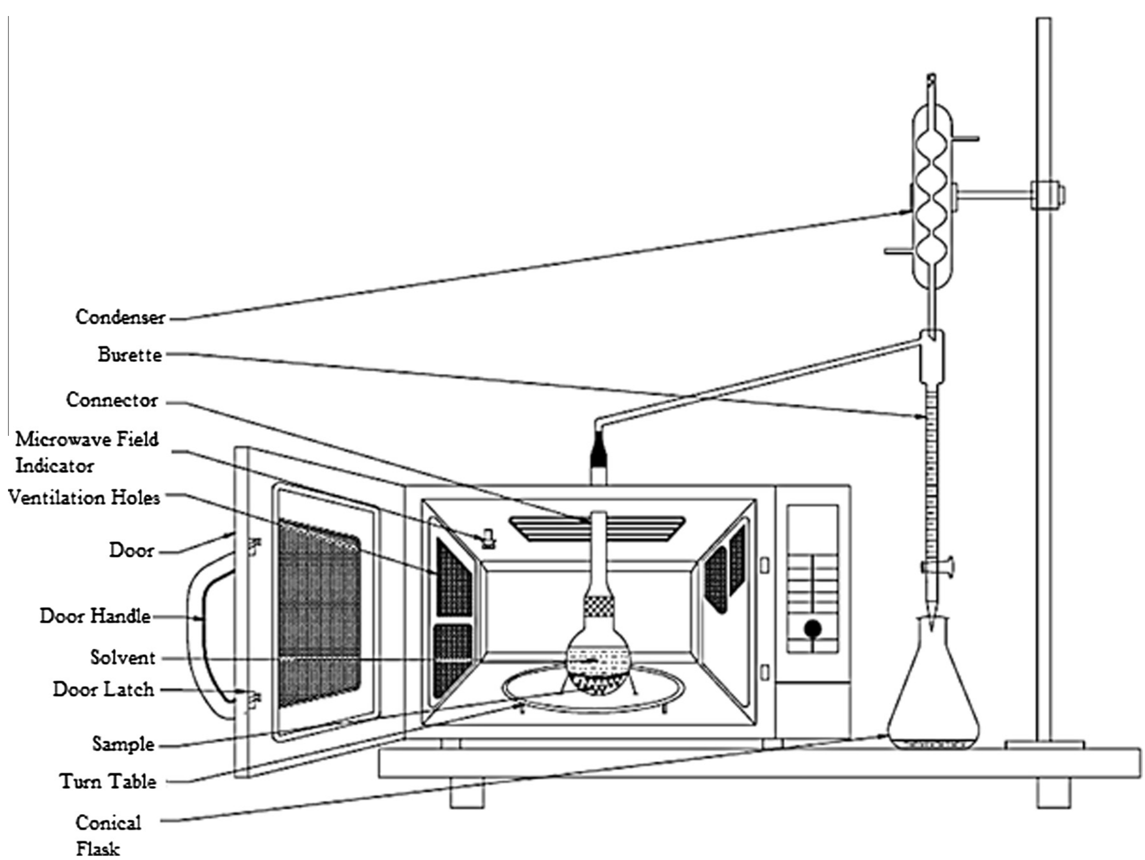


**Figure 1** Setup for MAE of bioactive compounds from *A. vasica* and *C. citratus*.

**Table 1** Empirical models, constants and regressed statistical parameters for drying of *A. vasica* and *C. citratus*.

| No. | Model name and expression | Model constants | | Statistical parameters | | |
|---|---|---|---|---|---|---|
| | | *A. vasica* | *C. citratus* | | *A. vasica* | *C. citratus* |
| 1 | Newton $MR = \exp(-kt)$ | $k = 0.0088$ | $k = 0.0251$ | $RSS$ | 0.0030 | 0.0018 |
| | | | | $E_{RMS}$ | 0.0550 | 0.0421 |
| | | | | $\chi^2$ | 0.0031 | 0.0019 |
| | | | | $R^2$ | 0.9618 | 0.9728 |
| 2 | Page $MR = \exp(-kt^n)$ | $k = 0.0110$ | $k = 6.5 \times 10^{-05}$ | $RSS$ | 0.0071 | 0.0001 |
| | | $n = 1.0000$ | $n = 1.5854$ | $E_{RMS}$ | 0.0846 | 0.0103 |
| | | | | $\chi^2$ | 0.0076 | 0.0001 |
| | | | | $R^2$ | 0.9096 | 0.9087 |
| 3 | Henderson $MR = a \cdot \exp(-kt)$ | $k = 0.0112$ | $k = 0.0028$ | $RSS$ | 0.0076 | 0.0012 |
| | | $a = 1.0011$ | $a = 1.1488$ | $E_{RMS}$ | 0.0877 | 0.0352 |
| | | | | $\chi^2$ | 0.0082 | 0.0013 |
| | | | | $R^2$ | 0.9029 | 0.9154 |
| 4 | Logarithmic $MR = a \cdot \exp(-kt) + c$ | $k = 0.0107$ | $k = 0.0003$ | $RSS$ | 0.0037 | 0.0003 |
| | | $a = 1.0170$ | $a = 1.4583$ | $E_{RMS}$ | 0.0611 | 0.0162 |
| | | $c = 0.0180$ | $c = -0.4250$ | $\chi^2$ | 0.0041 | 0.0003 |
| | | | | $R^2$ | 0.9528 | 0.9673 |
| 5 | Wang and Singh $MR = 1 + at + bt^2$ | | | $RSS$ | 0.0052 | 0.0042 |
| | | $a = -0.0076$ | $a = -0.0035$ | $E_{RMS}$ | 0.0724 | 0.0646 |
| | | $b = 1.46 \times 10^{-05}$ | $b = 3.1 \times 10^{-06}$ | $\chi^2$ | 0.0056 | 0.0078 |
| | | | | $R^2$ | 0.9338 | 0.9377 |
| 6 | Diffusion $MR = a \cdot \exp(-kt) + (1-a) \cdot \exp(-kbt)$ | $k = 0.0110$ | $k = 0.0115$ | $RSS$ | 0.0071 | 0.0001 |
| | | $a = 0.0999$ | $a = -15.720$ | $E_{RMS}$ | 0.0846 | 0.0118 |
| | | $b = 1.0000$ | $b = 0.9301$ | $\chi^2$ | 0.0079 | 0.0002 |
| | | | | $R^2$ | 0.9096 | 0.8988 |
| 7 | Verma $MR = a \cdot \exp(-kt) + (1-a) \cdot \exp(-gt)$ | $k = 0.0061$ | $k = 0.0170$ | $RSS$ | 0.0026 | 0.0016 |
| | | $a = 2.7141$ | $a = -8.9498$ | $E_{RMS}$ | 0.0518 | 0.0403 |
| | | $g = 0.0049$ | $g = 0.0177$ | $\chi^2$ | 0.0029 | 0.0019 |
| | | | | $R^2$ | 0.9660 | 0.9751 |
| 8 | Two term exponential $MR = a \cdot \exp(-kt) + (1-a) \cdot \exp(-kat)$ | | | $RSS$ | 0.0026 | 0.0018 |
| | | $k = 0.0105$ | $k = 1293.54$ | $E_{RMS}$ | 0.0512 | 0.0421 |
| | | $a = 1.6502$ | $a = 1.9 \times 10^{-05}$ | $\chi^2$ | 0.0028 | 0.0020 |
| | | | | $R^2$ | 0.9669 | 0.9728 |
| 9 | Midilli $MR = a \cdot \exp(-kt^n) + bt$ | $k = 9.9\text{E}{-06}$ | $k = -0.0634$ | $RSS$ | **0.000082** | **0.0001** |
| | | $a = 0.9602$ | $a = 0.9914$ | $E_{RMS}$ | **0.0090** | **0.0117** |
| | | $n = 1.7607$ | $n = 0.9786$ | $\chi^2$ | **0.000073** | **0.0002** |
| | | $b = 9.8 \times 10^{-06}$ | $b = -0.0580$ | $R^2$ | **0.9991** | **0.9984** |
| 10 | Two term $MR = a \cdot \exp(-k_1 t) + b \cdot \exp(-k_2 t)$ | $k_1 = 0.0091$ | $k_1 = 0.0257$ | $RSS$ | 0.0019 | 0.0017 |
| | | $k_2 = 0.0088$ | $k_2 = 0.0257$ | $E_{RMS}$ | 0.0439 | 0.0414 |
| | | $a = 5.0091$ | $a = 0.5163$ | $\chi^2$ | 0.0022 | 0.0022 |
| | | $b = -3.9150$ | $b = 0.5163$ | $R^2$ | 0.9756 | 0.9737 |

[*] Note: Values marked in bold show applicability of Midilli equation.

water/g dry solids. To determine an empirical mathematical model to represent the effect of MW output power on the constants and coefficients, all ten models were derived into $M^N$ number of new models using Arrhenius, Exponential and Linear type expressions. $N$ is the total number of constants and coefficients in the model and $M$ is the number of combination equations. The root mean square error ($E_{RMS}$), residual sum of squares ($RSS$) and chi-square ($\chi^2$) were used as the primary criteria to select the equation that best expresses the MW drying curves (Eq. (2)–(4)). $MR_{exp,i}$ and $MR_{pre,i}$ are the '$i$th' experimental and predicted moisture ratio, respectively; $n$ is the number of observations and $N$ is the number of constants in drying model.

$$RSS = \sum_{i=1}^{n} \left(MR_{exp,i} - MR_{pred,i}\right)^2 \tag{2}$$

$$E_{RMS} = \left[\frac{1}{n}\sum_{i=1}^{n}\left(MR_{exp,i} - MR_{pred,i}\right)^2\right]^{1/2} \tag{3}$$

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pred,i}\right)^2}{n - N} \tag{4}$$

The MW drying kinetics was evaluated on the basis of loss of leaf mass. Mathematical differentiation of the drying kinetics allowed the determination of drying rates [17]. An analysis of the falling rate period was carried out to determine the

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effective moisture diffusivity ($D_{eff}$) as well as the influence of process variables on it. According to Fick's law the non-steady state diffusion can be expressed by Eq. (5) where, $D_{eff}$ is the moisture diffusivity ($m^2\,s^{-1}$), $L$ is half the thickness of the sample and $t$ is the drying time (s). The linearized form of Eq. (5) is expressed in Eq. (6).

$$MR = \left(\frac{8}{\pi^2}\right) \exp\left(\frac{-\pi^2 D_{eff} t}{4L^2}\right) \quad (5)$$

$$\ln MR = \ln\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 D_{eff} t}{4L^2} \quad (6)$$

The following assumptions were made: (i) moisture is uniformly distributed throughout the sample; (ii) mass transfer is symmetric with respect to the center of the leaf; (iii) surface moisture content instantaneously reaches equilibrium with the ambient surrounding and (iv) resistance to mass transfer at the surface is negligible compared to the internal resistance of the sample. The linearized dependency of effective diffusivity of the leaves on MW power and sample mass is represented by Eq. (7). $E_a$ is the activation energy ($W\,g^{-1}$), $m$ is the sample mass (g) and $P$ is the MW output power (W).

$$\ln D_{eff} = \ln D_o - \frac{E_a m}{P} \quad (7)$$

### 2.3. Characterization

The structure of both fresh and dehydrated leaves was observed through a scanning electron microscope (FEI Quanta FEG200, Japan). Samples were coated with gold to provide a reflective surface for the electron beam (20 kV). Fourier Transform Infra-Red (FTIR) spectra were recorded using a Perkin Elmer spectrometer (RX1, USA) between 4000 and 400 $cm^{-1}$ and scan rate of minimum 20 cycles to detect surface organic structures.

## 3. Results and discussion

### 3.1. Influence of process variables

The effect of MW power was investigated at three output powers. The time for establishment of drying equilibrium from an initial moisture content of 70.72% for *A. vasica* was found to be 180, 260 and 780 s at 300, 180 and 100 W respectively (Fig. 2(a)). In contrast, the drying time for *C. citratus* (initial moisture of 68.75%) increased as 300, 960 and 4200 s when MW power decreased from 300 W to 100 W (Fig. 2(b)). As expected, the time for drying was inversely proportional to the MW output power levels applied. For *C. citratus*, a decrease of 66.67% in drying time is seen as against 77.25% in *A. vasica* when MW power is increased from 100 to 180 W. In comparison, the decrease in time is less significant when power is further increased to 300 W for both leaves. The entire process was governed by internal diffusion as it was restricted to falling-rate drying with the absence of a constant rate drying period evident from the curves [16]. High initial moisture content could have eased moisture removal in the early stages although this ceased at later stages when the drying approached equilibrium moisture. Analysis of the experimental results for the effect of sample loading indicates that

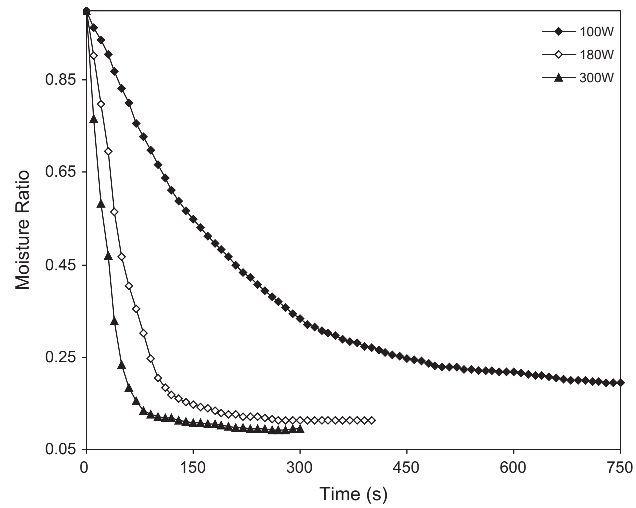


**Figure 2a** Drying curves for *A. vasica* under influence of MW power at sample loading of 10 g.

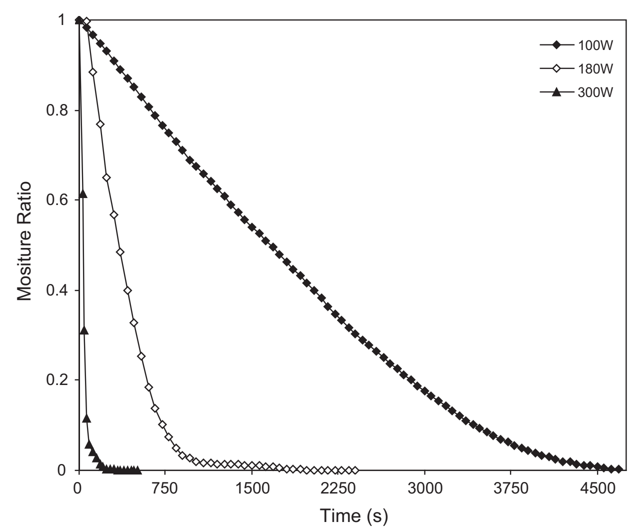


**Figure 2b** Drying curves for *C. citratus* under influence of MW power at sample loading of 50 g.

the initial mass had a significant impact on drying time and rate. During the drying of *A. vasica,* increasing the mass from 10 to 50 g at 300 W caused drying time to increase from 180 to 240 s (Fig. 3(a)). Similarly, for *C. citratus* at 180 W, drying time increased from 450 to 960 s with increasing sample loading (Fig. 3(b)). Therefore, in both leaves the rate of MW drying and sample loading followed an inverse relationship [16].

### 3.2. Mathematical modeling of drying curves

Regression of the experimental data against all the ten empirical drying models indicated that the Midilli equation best described the drying kinetics for both *A. vasica* and *C. citratus*. This was concluded based on high $R^2$ (0.999, 0.998), low $RSS$ ($8.2 \times 10^{-5}$, $1.36 \times 10^{-4}$), low $E_{RMS}$ (0.009, 0.011) and low $\chi^2$

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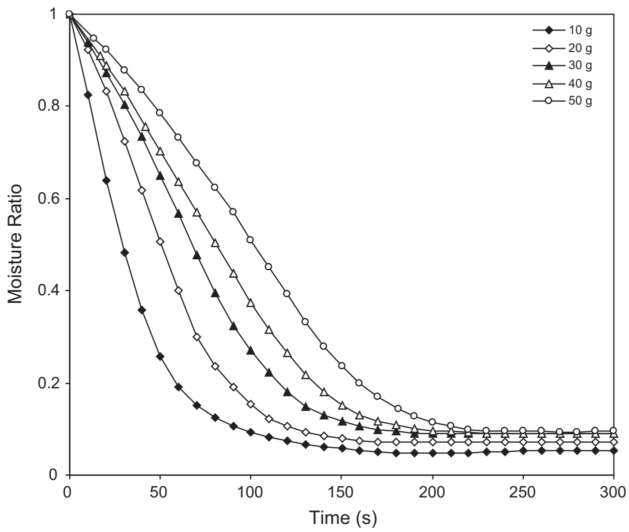


**Figure 3a** Drying curves for *A. vasica* under influence of sample loading at 300 W.

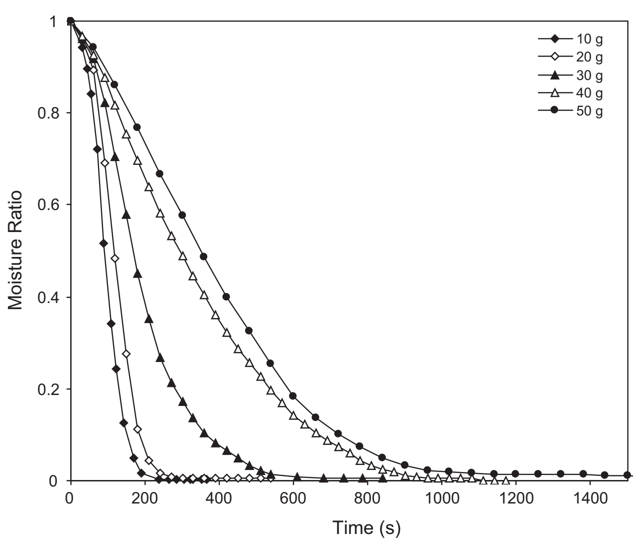


**Figure 3b** Drying curves for *C. citratus* under influence of sample loading at 180 W.

($7.35 \times 10^{-5}$, 0.002) values (Table 1). Henceforth, the Midilli equation was considered for further study and 81 equations[4] were developed as per $M^N$ combinations for both leaves. Multiple regression analysis of the kinetic data against the 81 modified Midilli equations allowed Eq. (8) (*A. vasica*) and Eq. (9) (*C. citratus*) to be concluded as the best fits.

$$MR = \left(1.0375 \cdot \exp\frac{-0.9997}{8.314P}\right)\exp(-0.9996 \cdot \exp(-0.0501P)) \times \left(t^{0.9359\cdot\exp\frac{-8.3\times10^{-5}}{8.314}}\right) + \left(0.0002 \cdot \exp\frac{-0.00023}{8.314P}\right)t \qquad (8)$$

[4] The Midilli equation modified with Arrhenius, Exponential and Linear type expressions resulted in 81 equations and has been presented as Supplementary Table S1.

$$MR = \left(0.2105 \cdot \exp\frac{-0.0735}{8.314P}\right)\exp(-0.0208 \cdot \exp(-1.16 \times 10^{-6} \cdot P)) \times \left(t^{0.0948\cdot\exp\frac{-0.1278}{8.314}}\right) - \left(9.7 \times 10^{-5} \cdot \exp\frac{-9.7 \times 10^{-5}}{8.314P}\right)t \qquad (9)$$

Subsequently, the derived model equations were validated by comparing the predicted and experimental moisture ratios; the coefficient of determination was found to be 0.9995 (Eq. (8)) and 0.9994 (Eq. (9)) confirming the model's accuracy and suitability to describe the drying behavior.

### 3.3. Effective moisture diffusivity and activation energy

The method of slopes was used for plots based on Eq. (6) to determine the effective moisture diffusivity at different MW power and sample loading. The calculated values have been reported in Table 2. For both leaves increasing MW power results in higher diffusivity while sample loading exhibits an inverse relationship. The maximum $D_{eff}$ value was $5.27 \times 10^{-10}$ m$^2$ s$^{-1}$ for *A. vasica* at 300 W and 10 g sample loading. Similarly, the maximum $D_{eff}$ at 180 W for *C. citratus* was observed at the minimum loading to be $7.75 \times 10^{-09}$ m$^2$ s$^{-1}$. The supposition here is that the combination of smaller sample mass and higher MW power increases vapor pressure within the leaves allowing better transfer of heat energy and results in greater moisture diffusivity [26]. It must be acknowledged that at lower MW output power and higher sample loads, there was small deviation from linearity which could be a result of non-uniform distribution of initial moisture in the leaves and/or shrinkage of the product [23]. The activation energies were estimated through plots based on Eq. (7) and were found to be 31.88 and 9.08 W g$^{-1}$ with pre-exponential ($D_0$) factor determined as $1.42 \times 10^{-14}$ and $1.32 \times 10^{-08}$ for *A. vasica* and *C. citratus*, respectively. The linearity of the plots suggested the possibility of Arrhenius dependence. This was verified through a plot based on the exponential expression of the Arrhenius equation as in Eq. (10) [16]. The drying rate constant ($k$; min$^{-1}$) was obtained from Eqs. (8) and (9) to estimate the activation energy ($E_a$) and these values were found to be similar to that obtained earlier using Eq. (7).

**Table 2** Effective moisture diffusivity estimations and regression coefficients for *A. vasica* and *C. citratus*.

| Power (W) | Sample load (g) | $D_{eff}$ (m$^2$ s$^{-1}$) $\times 10^{10}$ | $R^2$ |
|---|---|---|---|
| *A. vasica* | | | |
| 100 | 10 | 0.63 | 0.9008 |
| 180 | 10 | 2.69 | 0.9187 |
| 300 | 10 | 5.27 | 0.9391 |
| 300 | 20 | 4.31 | 0.9669 |
| 300 | 30 | 3.80 | 0.9845 |
| 300 | 40 | 3.42 | 0.9736 |
| 300 | 50 | 2.63 | 0.9483 |
| *C. citratus* | | | |
| 100 | 50 | 1.60 | 0.9498 |
| 180 | 50 | 7.30 | 0.9644 |
| 300 | 50 | 37.4 | 0.9769 |
| 180 | 20 | 77.5 | 0.9421 |
| 180 | 30 | 51.4 | 0.9277 |
| 180 | 40 | 38.7 | 0.9215 |
| 180 | 50 | 22.6 | 0.9173 |

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**Table 3** Comparing the conventional Soxhlet extraction and MAE yields of bioactive compounds from *A. vasica and C. citratus*.

| Sample load (g) | Sample:Solvent | % Extract yield | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | *A. vasica* | | | | *C. citratus* | | | |
| | | Soxhlet extraction | MAE (MW output power) | | | Soxhlet extraction | MAE (MW output power) | | |
| | | | 100 W | 180 W | 300 W | | 100 W | 180 W | 300 W |
| 10 | 1:10 | 36.11 | 32.72 | 30.66 | 29.25 | 26.23 | 22.00 | 25.00 | 27.00 |
| | 1:15 | 38.47 | 33.15 | 30.45 | 28.85 | 31.27 | 24.80 | 26.84 | 30.01 |
| | 1:20 | **40.28** | **37.83** | **34.64** | **32.71** | 32.05 | 27.12 | 28.27 | 30.54 |
| 20 | 1:10 | 34.78 | 29.89 | 27.95 | 26.75 | 24.88 | 25.60 | 27.20 | 28.50 |
| | 1:15 | 35.76 | 31.07 | 28.60 | 27.09 | 29.54 | 27.23 | 29.89 | 29.79 |
| | 1:20 | 38.24 | 33.60 | 30.51 | 28.75 | **30.87** | **28.78** | **30.78** | **31.24** |
| 30 | 1:10 | 30.38 | 23.29 | 21.42 | 20.29 | 23.11 | 21.30 | 23.50 | 24.00 |
| | 1:15 | 31.02 | 24.45 | 22.05 | 20.58 | 24.36 | 23.12 | 25.87 | 26.87 |
| | 1:20 | 33.79 | 27.83 | 24.87 | 23.17 | 28.38 | 26.01 | 28.52 | 29.75 |
| 40 | 1:10 | 21.47 | 12.08 | 10.29 | 9.220 | 20.56 | 14.90 | 16.80 | 18.80 |
| | 1:15 | 22.89 | 13.76 | 11.39 | 9.990 | 23.74 | 17.51 | 18.99 | 20.91 |
| | 1:20 | 24.09 | 15.49 | 12.67 | 11.03 | 25.19 | 19.59 | 21.23 | 23.45 |
| 50 | 1:10 | 16.34 | 7.910 | 6.310 | 5.290 | 18.22 | 9.601 | 12.10 | 13.50 |
| | 1:15 | 17.10 | 9.340 | 6.990 | 5.650 | 19.97 | 11.22 | 14.89 | 15.74 |
| | 1:20 | 19.74 | 9.980 | 7.240 | 5.670 | 20.35 | 15.11 | 16.41 | 17.84 |

** Note: Values marked in bold show optimum values.

$$\ln k = \ln k_0 - \frac{-E_a m}{P} \quad (10)$$

### 3.4. Extraction

Extraction was performed on leaves dried under optimal MW conditions that were determined by the modified Midilli equations (Eqs. (8) and (9)). For *A. vasica and C. citratus this was determined to be* 100 W, 40 g and 180 W, 20 g respectively. Following MW drying both the leaves were subjected to conventional Soxhlet extraction and MAE. The results for the extraction runs have been summarized in Table 3. It was observed that increasing the initial sample loading during extraction at a constant sample to solvent ratio resulted in a trend of decreasing extract yield for both Soxhlet and MAE (at a constant MW power). For instance, at 100 W and fixed sample/solvent ratio of 1:10, as sample loading of *A. vasica* was increased from 10 to 50 g, the extract yield more than halved from 36.1% to 16.3% for Soxhlet extraction and dropped from 32.7% to 7.91% during MAE. At all solvent ratios the sample loading exhibited an inverse relationship with extract yield for both the leaves. At fixed sample loading, varying the sample/solvent ratio resulted in increased extract yield for both processes. *A. vasica* recorded a 15.61% increase in MAE yield when the ratio was changed from 1:10 to 1:20 at 10 g loading and 100 W output power while *C. citratus* extracted under the same conditions with the Soxhlet apparatus indicated a 22.15% increase in yield. Increasing the solvent volume at fixed sample mass is favorable as it increases extraction efficiency due to greater probability of contact with the plant cellular matrix [27].

Microwave power influenced the extraction significantly although contrary trends were recorded for both leaves. Irrespective of the other process variables during MAE, *A. vasica* recorded decreasing yields while *C. citratus* depicted increasing yields as MW power was varied from 100 to 180 W. Enhancing the MW power may result in physical damage such as scorching, over-heating, charring and uneven temperature distribution [1]. Although visible damage was not observed under the investigated conditions in the present study, it may be possible that the continuous uneven rise of local temperature and concurrent reduction of the leaf material with loss of moisture could have resulted in reduced yields. This study thus concludes 100 W to be sufficient output power for MAE of *A. vasica*.

Conversely, enhanced yields were observed for *C. citratus* when MW power was increased from 100 to 300 W; optimum extract yield (31.24%) occurred at 300 W output power, sample load of 20 g and sample/solvent ratio of 1:20. The accelerated extraction with increasing MW power is probably a result of interaction of microwave energy with leaf biomolecules by dipole rotation and ionic conduction [11]. Dried leaves contain a residual albeit minute amount of moisture which readily absorbs microwave energy during MAE converting it into heat energy when they evaporate. Evaporation of moisture and subsequently, the solvent itself enhances the pressure within the cell walls eventually rupturing it and leaching the target compounds [15]. In comparison with MAE, the Soxhlet apparatus produced a higher extract yield (6.08%) for *A. vasica* but a lower yield (7.26%) for *C. citratus*; average extraction time for the Soxhlet process was 10 h and 8.5 h while the time for MAE at 300 W was 210 s and 150 s, respectively. These results are in line with those in the literature [18,19]. Specifically, good agreement of results and trends is seen with Pan et al. [19] who comparatively studied MAE and Soxhlet extraction of polyphenols and caffeine from green tea leaves.

### 3.5. Characterization

The influence of MW on the drying of leaves was observed using SEM before and after irradiation at 300 W. As Fig. 4 depicts, MW irradiation caused significant changes in surface

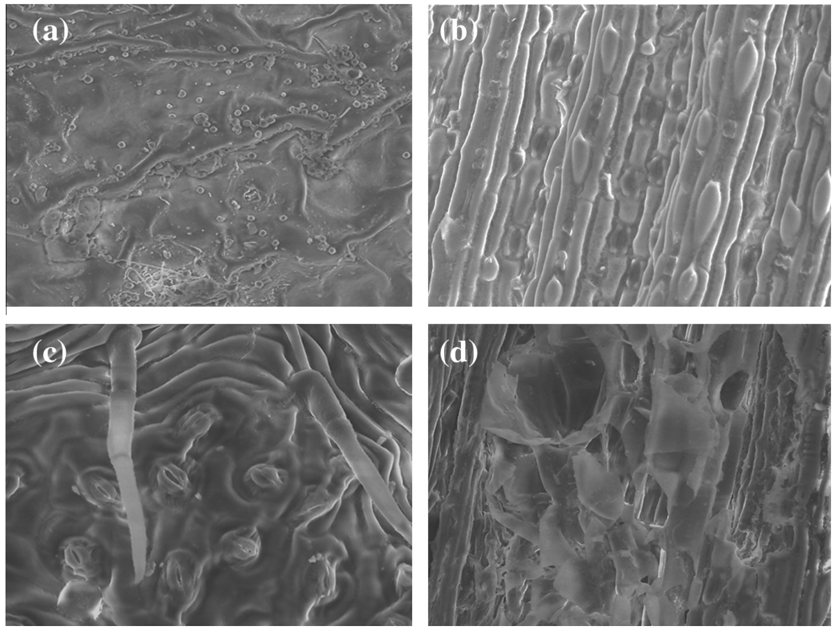


**Figure 4** SEM images (20 kV) for *A. vasica* at 1200 X (a) fresh leaves and (b) MW irradiated at 300 W; *C. citratus* at 800 X (c) fresh leaves and (d) MW irradiated at 300 W.

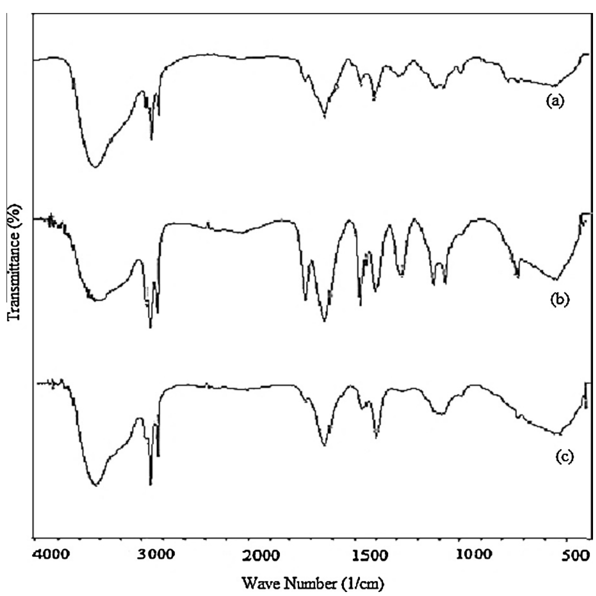


**Figure 5** FTIR spectrogram of leaf extracts from *A. vasica* at different microwave output powers: (a) 100 W, (b) 180 W and (c) 300 W.

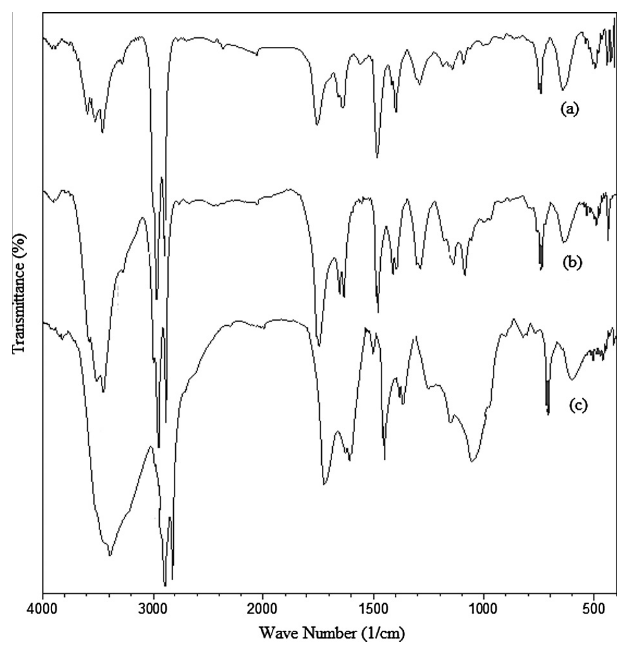


**Figure 6** FTIR spectrogram of leaf extracts from *C. citratus* at different microwave output powers: (a) 100 W, (b) 180 W and (c) 300 W.

morphology relative to microstructure of the untreated leaves. No pores or open structures were evident in the untreated leaves Fig. 4(a and c). However, irradiation clearly resulted in a relatively porous structure due to rapid vaporization of leaf moisture. As seen in Fig. 4(b and d), heat generation occurred in the bulk of the sample and was transported thereafter from the bulk to surrounding parts. Such temperature gradients are only seen when MW energy is applied to drying applications. Moreover, the emergence of the spore stalk matrix from the stoma and guard cells on the leaf epidermis was recorded by the SEM images.

FTIR spectra of the leaf extract under MAE are shown in Figs. 5 and 6. For *A. vasica* the bands at 2918 and 2848 $cm^{-1}$ pertain to symmetric stretching vibration of aliphatic ($–CH_2$) group. The presence of hydroxyl groups was seen through the OH– stretching between 3450 and 3429 $cm^{-1}$. With increasing MW power, the intensity of peaks at 2326, 2035 and 1877 $cm^{-1}$ increased. However, vibrations at 1724 $cm^{-1}$ (aldehydes) depicted reduced transmittance which could be an indication of the formation of new carbonyl groups. The main peaks at 3450, 3441, 2918, 2848, 1726, 1631 and 1462 $cm^{-1}$ however, did not change significantly with increasing MW output power. The spectrum recorded for *C. citratus* (Fig. 6) showed similar trends with major bands at 3460, 2916, 1732, 1618, 1463 and 1006 $cm^{-1}$.

## 4. Conclusions

In the present study, the microwave drying behavior of two pharmaceutically important medicinal leaves, *A. vasica* and *C. citratus* was investigated. A two-step modeling approach was undertaken: (i) non-linear regression analysis of the experimental data against conventional drying models indicated that the Midilli equation best suits both leaves and (ii) further improvisation was done to derive 81 semi-empirical Midilli equations which were regressed to allow the determination of a characteristic drying equation for each leaf. Following the analysis of drying characteristic of the leaves, a comparative study was undertaken to study the MAE and conventional Soxhlet extraction of bioactive compounds present in the MW dried leaves. Results indicated that extract yield was similar to the Soxhlet setup for *A. vasica* although a drastic reduction in time can be attained with MAE (210 s) as against an average Soxhlet extraction time of 10 h. Moreover, the extract yield for MAE of *C. citratus* was higher than the conventional process with optimal parameters determined to be 20 g sample load, 1:20 sample/solvent ratio, extraction time of 150 s and 300 W output power. The derived model equations, parameters and process detailed here can be used an operational guide for the drying and extraction of bioactive compounds from *A. vasica* and *C. citratus*.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.aej.2015.12.020.

## References

[1] G.R. Askari, Z. Emam-Djomeh, S.M. Mousavi, An investigation of the effects of drying methods and conditions on drying characteristics and quality attributes of agricultural products during hot air and hot air/microwave-assisted dehydration, Dry. Technol. 27 (7–8) (2009) 831–841.
[2] C.K. Atal, Chemistry and pharmacology of vasicine: A new Oxytocic and abortifacient, Indian Drugs 15 (2) (1980) 15–18.
[3] B. Balakrishnan, S. Paramasivam, A. Arulkumar, Evaluation of the lemongrass plant (*Cymbopogon* citratus) extracted in different solvents for antioxidant and antibacterial activity against human pathogens, Asian Pac. J. Trop. Dis. 4 (2014) S134–S139.
[4] B. Bayramoglu, S. Sahin, G. Sumnu, Solvent-free microwave extraction of essential oil from oregano, J. Food Eng. 88 (4) (2008) 535–540.
[5] C.H. Chan, R. Yusoff, G.C. Ngoh, F.W. Kung, Microwave-assisted extractions of active ingredients from plants, J. Chromatogr. A 1218 (37) (2011) 6213–6215.
[6] U.P. Claeson, T.G. Malmfors, Wikman, J.G. Bruhn, Adhatoda vasica: a critical review of ethno-pharmacological and toxicological data, J. Ethnopharmacol. 72 (1–2) (2000) 1–20.
[7] S.S. Costa, Y. Gariepy, S.C.S. Rocha, V. Raghavan, Microwave extraction of mint essential oil-temperature calibration for the oven, J. Food Eng. 126 (2014) 1–6.
[8] K.J. Deepak, L. Panda, P. Lavanya, S. Ramaiah, A. Anbarasu, Detection and confirmation of alkaloids in leaves of *Justicia adhatoda* and bioinformatics approach to elicit its anti-tuberculosis activity, Appl. Biochem. Biotechnol. 168 (5) (2012) 980–990.
[9] M. Ganesapillai, I. Regupathi, T. Murugesan, An empirical model for the estimation of moisture ratio during microwave drying of plaster of paris, Dry. Technol. 26 (7) (2008) 963–978.
[10] M. Ganesapillai, I. Regupathi, T. Murugesan, Modeling of thin layer drying of banana (Nendran Spp) under microwave, convective and combined microwave-convective processes, Chem. Prod. Process Model. 6 (1) (2011).
[11] M. Gfrerer, E. Lankmayr, Screening, optimization and validation of microwave assisted extraction for the determination of persistent organochlorine pesticides, Anal. Chim. Acta 533 (2005) 203–211.
[12] J. Gómez-Estaca, C. López-de-Dicastillo, P. Hernández-Muñoz, R. Catalá, R. Gavara, Advances in antioxidant active food packaging, Trends Food Sci. Technol. 35 (1) (2014) 42–51.
[13] B. Hiranvarachat, S. Devahastin, Enhancement of microwave-assisted extraction via intermittent radiation: extraction of carotenoids from carrot peels, J. Food Eng. (2014) 17–26.
[14] G. Hong, H. Yi-Na, B. Gao, Peng. Li, C. Inagaki, J. Kawabata, Inhibitory effect on α-glucosidase by Adhatoda vasica Nees, Food Chem. 108 (3) (2008) 965–972.
[15] V. Mandal, Y. Mohan, S. Hemalatha, Microwave assisted extraction—an innovative and promising extraction tool for medicinal plant research, Pharmacognosy Rev. 1 (1) (2007) 7–18.
[16] B. Ozbek, G. Dadali, Thin-layer drying characteristics and modelling of mint leaves undergoing microwave treatment, J. Food Eng. 83 (4) (2007) 541–549.
[17] S. Pabis, D.S. Jayas, S. Cenkowski, Grain Drying: Theory and Practice, John Wiley and Sons, 1998, ISBN 978-0-471-57387-6.
[18] X. Pan, H. Liu, G. Jia, Y.Y. Shu, Microwave-assisted extraction of glycyrrhizic acid from licorice root, Biochem. Eng. J. 5 (3) (2000) 173–177.
[19] X. Pan, G. Niu, H. Liu, Microwave-assisted extraction of tea polyphenols and tea caffeine from green tea leaves, Chem. Eng. Process. 42 (2) (2003) 129–133.
[20] L. Paviani, S.B.C. Pergher, C. Dariva, Application of molecular sieves in the fractionation of lemongrass oil from high-pressure carbon dioxide extraction, Braz. J. Chem. Eng. 23 (2006) 219–225.
[21] N. Ratola, S. Lacorte, D. Barceló, A. Alves, Microwave-assisted extraction and ultrasonic extraction to determine polycyclic aromatic hydrocarbons in needles and bark of *Pinus pinaster Ait*. and *Pinus pinea L*. by GC–MS, Talanta 77 (3) (2009) 1120–1128.
[22] W. Routray, V. Orsat, Microwave-assisted extraction of flavonoids: a review, Food Bioprocess Technol. 5 (2) (2012) 409–424.
[23] G.P. Sharma, S. Prasad, Effective moisture diffusivity of garlic cloves undergoing microwave-convective drying, J. Food Eng. 65 (4) (2004) 609–617.
[24] B. Singh, R.A. Sharma, Anti-inflammatory and anti-microbial properties of *Pyrroloquinazoline* alkaloids from *Adhatoda vasica Nees*, Phytomedicine 20 (5) (2013) 441–445.
[25] A. Tahmasebi, J. Yu, Y. Han, H. Zhao, S. Bhattacharya, Kinetic study of microwave and fluidized-bed drying of Chinese lignite, Chem. Eng. Res. Des. 92 (2014) 54–65.
[26] S.V. Venkata Raman, S. Iniyan, R. Goic, A review of solar drying technologies, Renew. Sustain. Energy Rev. 16 (5) (2012) 2652–2670.

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[27] W. Xiao, L. Han, B. Shi, Microwave-assisted extraction of flavonoids from *Radix astragali*, Sep. Purif. Technol. 62 (3) (2008) 614–618.

[28] M. Zarein, S.H. Samadi, B. Ghobadian, Investigation of microwave dryer effect on energy efficiency during of apple slices, J. Sau. Soc. Agric., 2014 (in press). doi: 10.1016/j.jssas.2013.06.002.

[29] M. Ganesapillai, M. Mathew, A. Singh, P. Simha, Influence of microwave and ultrasound pretreatment on solvent extraction of bio-components from walnut (Julgans regia L.) shells, Period. Polytech. Chem. Eng. 60 (1) (2015) 40–48, http://dx.doi.org/10.3311/PPch.8480.